METHOD FOR PREPARING HIGH-PURITY GERMANIUM HYDRIDE

The invention now proposed relates to the preparation of germanium-containing materials and concerns the development of an electrochemical method for preparing high-purity germanium hydride, suitable for use as a source of germanium in microelectronics technologies.

A method is known for preparing germanium hydride by electrolysis of an aqueous-alkaline solution, containing 25-35 g/l of germanium dioxide, at a nickel cathode in a diaphragm cell at a current density of 1.0-1.5 A/cm^2, electrolysis being performed with cross-mixing of electrolyte streams, feeding electrolyte from the cathode chamber, after removal of germanium hydride and hydrogen, into the anode chamber, and a stream of electrolyte from the anode chamber, after removal of oxygen, into the cathode chamber (RF Patent No. 1732697, filed 19.01.90).

The method provides low productivity, of the order of 10 g/hour. The total content of the contaminants SiH_4, AsH_3, PH_3, H_2S, CH_4, Fe, Ni, Al, Ca, Mg, etc. in the resultant germanium hydride is not more than $1 \cdot 10^{-4}$%, which limits the field of its practical application, particularly for use in the production of epitaxial Si-Ge structures, where further improvement in the purity of the germanium hydride is needed.

The object on which the present invention is based, is to improve the purity of the germanium hydride and to improve the productivity of the method which is at the same time characterized by low energy content. This object is achieved in that, in a known method for preparing germanium hydride by electrolysis of an aqueous-alkaline solution, containing germanium dioxide, at a nickel cathode in a diaphragm cell at a current density of 1.0-1.5 A/cm^2 with subsequent isolation of the

germanium hydride from the mixture with hydrogen, the electrolysis being performed with cross-mixing of electrolyte streams, feeding electrolyte from the cathode chamber, after removal of germanium hydride and hydrogen, into the anode chamber, and a stream of electrolyte from the anode chamber, after removal of oxygen, into the cathode chamber, in accordance with the invention an electrical current is first passed through the aqueous-alkaline solution at a temperature no higher than 65°C for the time needed to achieve the minimum possible content of contaminants limiting for germanium hydride, after which germanium dioxide is added to the solution from a concentration of not less than 40 g/l to the solubility limit and electrolysis is performed at a temperature no higher than 65°C.

When preparing germanium hydride at the maximum possible productivity - 50 g/hour - it is desirable that electrolysis be performed at a germanium dioxide concentration of 50 g/l and an electrolyte temperature of 65°C.

The preparation of large volumes of germanium hydride is accompanied by high energy consumption owing to the fact that cooling and condensation when isolating germanium hydride from the mixture with hydrogen are performed at fairly low temperatures. Thus, in order to save energy when preparing large volumes of germanium hydride, it is desirable, before isolation of the germanium hydride, to concentrate the latter using a diffusion membrane. Concentration of the germanium hydride reduces the volume of hydrogen to be cooled, which leads to a reduction in energy consumption. Concentration of the hydride using said membrane is performed at room temperature.

A total content of the contaminants SiH_4, AsH_3, PH_3, H_2S, CH_4, Fe, Ni, Al, Ca, Mg, etc. in the germanium hydride isolated after synthesis at a level of not more than $1 \cdot 10^{-6}$% is acceptable for relatively wide fields of practical application, particularly as a source of germanium for nuclear radiation detectors.

Germanium hydride with a lower content of said contaminants is required for a number of fields of practical application. To achieve this, the isolated germanium hydride requires additional purification. Known methods of purification, such as rectification with a centre pot, ensure the removal of low- and high-boiling dissolved contaminants, and at the same time demand high energy expenditure. Thermodistillation ensures the removal of suspended particles and also demands high energy expenditure.

To prepare germanium hydride with a lower content of said contaminants and which at the same time does not demand additional energy expenditure, said object is achieved owing to the fact that, in a known method for preparing germanium hydride by electrolysis of an aqueous-alkaline solution, containing germanium dioxide, at a nickel cathode in a diaphragm cell at a current density of 1.0-1.5 A/cm^2 with subsequent isolation of the germanium hydride from the mixture with hydrogen, the electrolysis being performed with cross-mixing of electrolyte, feeding electrolyte from the cathode chamber, after removal of germanium hydride and hydrogen, into the anode chamber, and a stream of electrolyte from the anode chamber, after removal of oxygen, into the cathode chamber, in accordance with the invention an electrical current is first passed through the aqueous-alkaline solution at a temperature no higher than 65°C for the time needed to achieve the minimum possible content of contaminants limiting for germanium hydride, after which germanium dioxide is added to the solution from a concentration of not less than 40 g/l to the solubility limit and electrolysis is performed at a temperature no higher than 65°C, while the isolated germanium hydride is purified by the membrane method.

When preparing germanium hydride at the maximum possible productivity - 50 g/hour - it is desirable that electrolysis be performed at a germanium dioxide concentration of 50 g/l and an electrolyte temperature of 65°C.

When preparing large volumes of germanium hydride, it is desirable, before isolation, to concentrate the latter using a diffusion membrane.

In order to prepare germanium hydride with a total content of the contaminants SiH_4, AsH_3, PH_3, H_2S, CH_4, Fe, Ni, Al, Ca, Mg, etc. at a level of not more than $1 \cdot 10^{-7}$%, suitable for use as a germanium source in microelectronics technologies, it is preferable to purify the isolated germanium hydride using a gas-diffusion membrane, which ensures the simultaneous removal of molecular contaminants and contaminants in the form of metals.

Heterogeneous contaminants - suspended solid particles of submicron size - are limiting factors for a number of fields of practical application, such as, for example, optics and laser engineering. In order to remove the latter, purified germanium hydride is passed at room temperature through an ultrafiltration membrane, which ensures the removal of suspended particles of 0.05 μm size to a level of less than $5.5 \cdot 10^3$ particles/mole.

The abovementioned membranes may be made from polymeric material, or from metal, or from ceramic.

A novel aspect of the method is that an electrical current is passed through the aqueous-alkaline solution first, before addition of the germanium dioxide, which ensures the removal of the dissolved contaminants SiH_4, AsH_3, PH_3, H_2S, CH_4, etc., present in reagents and in the material of apparatus, which overall reduces more than 100-fold the content of the latter in the germanium hydride obtained after isolation, increasing the level of purification of the isolated germanium hydride by the membrane method. It is well known that hydrogen is liberated at the cathode when an electrical current is passed through an aqueous-alkaline solution. Analysis of the hydrogen for the content of the abovementioned contaminants is a criterion for the degree of removal of the contaminants from the electrolyte when performing electrolysis of an aqueous-alkaline solution.

Electrolysis is performed until the content of the limiting contaminants for the germanium hydride being prepared reaches the minimum possible content. The germanium dioxide concentration of not less than 40 g/l through to the solubility limit at an electrolyte temperature no higher than 65°C ensures a productivity of 40-50 g/hour, which is 4-5 times higher compared to the prior art. Productivity falls by a factor of 3 at a germanium dioxide concentration of less than 40 g/l. This is explained by the fact that, at a germanium dioxide concentration of less than 40 g/l, the rate of formation of germanium hydride falls as a consequence of its dependence on the concentration of germanium dioxide. Performing electrolysis at a temperature higher than 65° leads to a fall in the germanium hydride production rate owing to the increase in thermal decomposition of the latter at the abovementioned concentrations. The membrane method of purification is the cheapest and most efficient method. By virtue of the fact that the germanium hydride isolated after synthesis has a reasonably high level of purification, a total content of contaminants of not more than $1 \cdot 10^{-6}\%$, as mentioned above, the membrane method is readily implemented at room temperature, providing a more than 10-fold overall level of removal of molecular contaminants and metal contaminants, and removal of suspended particles of submicron size to a level of less than $5.5 \cdot 10^3$ particles/mole. If the germanium hydride isolated after synthesis contains contaminants with an overall content of more than $1 \cdot 10^{-6}\%$, as for example $1 \cdot 10^{-4}\%$ in the prior art, purification by the membrane method will be hindered, and for certain contaminants virtually impossible. The level of purification in the synthesis stage of germanium hydride which is to be further purified by the membrane method is thus an essential feature. All the features mentioned are essential both in the synthesis stage of germanium hydride and also in the stage of its purification, since each is necessary, and together they are sufficient for the preparation of

high-purity germanium hydride with the minimum possible energy expenditure.

The statements confirming the possibility of accomplishing the invention are supported by examples.

Example. Germanium hydride is prepared in a monopolar cell of filter-press type at a nickel cathode with a surface area of 500 cm^2. 2.5 N of KOH solution are poured into the cell and an electrical current is passed through at a density of 1.5 A/cm^2 and a temperature of 65°C until the content of the dissolved contaminants SiH_4, AsH_3, PH_3, H_2S, CH_4, etc., reaches the minimum possible content. The criterion for assessing the electrolysis performance time is the analysis of the hydrogen for the content of said contaminants. Germanium dioxide is then added to the aqueous-alkaline solution to a concentration of 50 g/l and electrolysis is performed at a temperature of 65°C. The electrodes are cooled with cold water during electrolysis. A cathode gas, which is separated off from the electrolyte, is formed at the cathode. The cathode gas consists of hydrogen and germanium hydride. According to the results of gas-chromatography analysis, the concentration of germanium hydride in the hydrogen stream is 6%. The gas mixture is fractionated and the germanium hydride is isolated. Before isolation, the hydride is concentrated using a gas-fractionating diffusion membrane such as PDMS - based on poly(arylate dimethylsiloxane) block copolymer, and is then isolated using the cryoscopic method.

According to the results of gas-chromatography and chemical-spectral methods of analysis, the total content of SiH_4, AsH_3, PH_3, H_2S, CH_4, Fe, Ni, Al, Ca, Mg, etc. in the germanium hydride isolated after synthesis is not more than $1 \cdot 10^{-6}$%. The productivity of the method is 50 g/hour.

Where necessary, when a higher level of removal of said contaminants is required, the prepared hydride is purified by the membrane method using a gas-diffusion membrane, which simultaneously ensures the removal of molecular contaminants and metal contaminants to a total

content of not more than $1 \cdot 10^{-7}\%$. The same membrane as for concentration of the germanium hydride may be used as the gas-diffusion membrane. Purification is performed at room temperature.

When the limiting contaminants are heterogeneous contaminants in the form of suspended solid particles of submicron size, supplementary purification of the germanium hydride is performed using ultrafiltration membranes, such as nuclear filters of lavsan. According to the results of ultramicroscope analysis, the content of said contaminants after purification is less than $5.5 \cdot 10^{3}$ particles/mole (for 0.05 μm particles).

The method now proposed for preparing high-purity germanium hydride, which includes electrochemical synthesis and purification of the isolated germanium hydride by the membrane method, provides high purification efficiency: the total content of SiH_4, AsH_3, PH_3, H_2S, CH_4, Fe, Ni, Al, Ca, Mg, etc. is not more than $1 \cdot 10^{-7}\%$, and the content of suspended particles of 0.05 μm in size is less than $5.5 \cdot 10^{3}$ particles/mole.

The productivity of the method is 40-50 g/hour, while the method is characterized by low energy expenditure, owing to the fact that concentration of the hydride in the stage of isolation from the mixture with hydrogen and purification of the isolated hydride are performed at room temperature.